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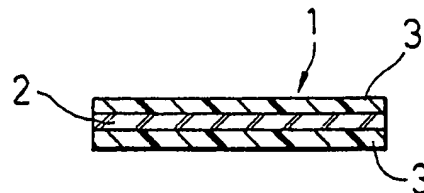
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(54) Preserving material and method for producing the same.

(57) A preserving material of a layered structure which is composed of an impregnated adsorbent sheet which contains a preserving liquid containing at least a lower alcohol and barrier films which cover the adsorbent sheet and which are impermeable to the preserving liquid. The effective components of the preserving liquid is evaporated little by little at least from the peripheral edges of the preserving material. This invention further relates to a method for producing the preserving material which consists of the steps of previously applying barrier films to both surfaces of an adsorbent sheet; and soaking the obtained layered material in the preserving liquid, thereby impregnating the adsorbent sheet with the preserving liquid from at least the edge portions of the layered material.

## FIG. 1



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## PRESERVING MATERIAL AND METHOD FOR PRODUCING THE SAME

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to a preserving material and a method for producing the same. More particularly, the invention relates to a preserving material which can maintain the freshness avoiding the deterioration of foodstuffs and the like. The preserving material of the present invention is characterized in that it can be easily sealed into packages of foodstuffs and the like to be preserved and the preserving liquid contained in the preserving material is not brought into direct contact with the goods to be preserved in packages. Furthermore, the present invention relates to a method for producing a preserving material continuously and inexpensively. The component layers of the preserving material are well bonded together and hardly peeled off.

#### 2. Description of the Prior Art

It has been well known that ethyl alcohol (ethanol) is useful for sterilizing or inhibiting the growth of microorganisms in order to preserve foodstuffs such as bread, fish, meat, fruits and vegetables.

For example, it is disclosed in Japanese Patent Publication No. 55-1787 that ethanol is directly sprayed to the surface of foodstuffs. Similar methods to use ethanol are disclosed also in U.S. Patent No. 3,908,031 and Canadian Patent No. 699,278.

These methods, however, even though the effect of preservation is good, are not desirable in view of external appearance and commercial value of foodstuffs because the natural qualities of foodstuffs are lost and flavors and coloring agents sometimes ooze out owing to the process that foodstuffs are applied with a thin layer of alcohol.

In Japanese Patent Publication No. 40-25228 and No. 55-2273, it is disclosed that ethanol is adsorbed by an adsorbent composed of the powders of starch, dextrin, gelatin, cellulose, silicon dioxide, aluminum silicate and talc and is sealed together with a foodstuff in a gas tight container.

In this method, however, because the bulky adsorbent powders such as starch and silicon dioxide are used and the surface areas of powders are very large, the rate of evaporation of the adsorbed alcohol is too large. Therefore, the effect of pres-

ervation cannot be maintained for a long period of time.

That is, in the case that the evaporation of alcohol from an adsorbent is too large, it is necessary that foodstuff packing is carried out soon after the adsorption of alcohol by an adsorbent, which causes difficulties in packing process. As disclosed in Japanese Patent Publication No. 55-2273, because the leakage of alcohol gas from packages of foodstuffs cannot be avoided completely, a long time preserving effect is not produced when packages are not replenished with alcohol. In other words, in order to maintain the concentration of alcohol above a certain level, it is preferable that the evaporation of alcohol is lower than a certain rate.

Furthermore, when foodstuffs are preserved using these ethanol-carrying powder, a bag or other container to hold the powder is inevitable, so that the process for packing foodstuffs is complicated to increase the packing cost. In addition, if the container for the adsorbent powder happen to break, the foodstuff in the package is contaminated with the adsorbent powder.

Besides the above references, there are many other references as follows:

a) Preservation of foodstuffs using ethanol and organic acids or their esters:  
Japanese Patent Publication No. 50-25531, No. 52-27217, No. 53-28485, No. 55-01787, No. 55-02274, No. 55-50674, No. 58-49156 and No. 58-49157, and U.S. Patent No. 4,550,026.

b) Preservation using ethanol and deoxidizing agents:

Japanese Patent Publication No. 57-79869, No. 57-079870 and No. 60-70053.

c) Preservation using ethanol in solid form:  
Japanese Patent Publication No. 60-184374, No. 62-69971 and No. 62-232365.

d) Preservation using deoxidizing agents:  
Japanese Patent Publication No. 48-11026, No. 50-04740, No. 51-34898, No. 53-33665, No. 55-44594, No. 57-18787, No. 58-29069, No. 59-32106, No. 60-30503, No. 60-30504, No. 60-31465, No. 60-35102, No. 60-36747, No. 61-17463, No. 61-36912, No. 61-36913 and No. 61-36914.

e) Preservation using other agents:  
British Patent No. 1,277,874 (propionic acid), U.S. Patent No. 3,346,398 (alkylene oxides), U.S. Patent No. 3,533,806 (carbon tetrachloride and glacial acetic acid), U.S. Patent No. 3,600,198 (propionic acid and benzoic acid), U.S. Patent No. 3,595,665 (acetic, propionic and formic acids), U.S. Patent Nos. 4,350,709 and 4,421,774 (sulfur dioxide, organic acid such as propionic acid and ammonia

gas), U.S. Patent No. 4,356,204 (ketoheanoic acids), U.S. Patent No. 4,404,040 ( $C_6$ - $C_{14}$  fatty acids), U.S. Patent No. Re. 32,416 (acid propionate salt), Australian Patent No. 102,824 ( $C_3$ - $C_{12}$  saturated aliphatic monocarboxylic acids) and Australian Patent No. 110,824 (halogenated hydrocarbon containing dichloromethyl group).

The above methods have several disadvantages in that some of them deprive foodstuffs of natural quality or flavor; they spoil external appearance of foodstuffs; the effect of preservation cannot be maintained for a long period of time; absorbent or adsorbent material and gastight container are required; and as mentioned in the foregoing, the process for the package of foodstuffs cannot be easy and simple and foodstuffs are liable to be contaminated by these preserving agents.

#### BRIEF SUMMARY OF THE INVENTION

It is, therefore, the object of the present invention to eliminate the above-described disadvantages in the conventional art.

That is, in accordance with the present invention, it is possible to prevent foodstuffs from the deterioration of taste caused by the direct contact with a preserving liquid and the contamination caused by the oozing out of flavors and coloring agents. Furthermore, the rate of evaporation of preserving liquid can be controlled for a long period of time so as to maintain the concentration of a preserving agent on a level suitable to avoid the growth of microorganisms. In addition, according to the present invention, the operation to soak an adsorbing material into a preserving liquid can be done easily in a short time and it is convenient that the preserving material of the invention can be simultaneously packed together with foodstuffs.

According to the present invention, the preserving material is characterized by a layered structure which is composed of an impregnated adsorbent sheet which contains a preserving liquid containing at least a lower alcohol and films which are impermeable to the preserving liquid (hereinafter referred to simply as "barrier films") which are applied to both surfaces of the impregnated adsorbent sheet. In the preserving material of the invention, the effective component of the preserving liquid is evaporated little by little from the peripheral edges of the preserving material.

In a modified embodiment of the present invention, at least one of the barrier films of the preserving material is provided with a plurality of small openings.

In another embodiment of the invention, the

peripheral edges of barrier films are bonded together.

In a further embodiment of the invention, at least one of the barrier films has a plurality of small openings and the peripheral edges of both of the barrier films which extend beyond the impregnated adsorbent sheet are thermally bonded together.

In still a further embodiment of the invention, the impregnated adsorbent sheet of the preserving material has a plurality of small openings and at least one of the barrier films also has a plurality of small openings.

The method for producing a preserving material consists of the steps of: previously applying barrier films to both surfaces of an adsorbent sheet; and soaking the obtained layered material in a preserving liquid which contains at least a lower alcohol, thereby impregnating the adsorbent sheet with the preserving liquid from at least the edge portions of the layered material.

#### BRIEF DESCRIPTION OF DRAWINGS

These and other objects and features of the present invention will become more apparent from the following description taken in connection with the accompanying drawings, in which:

Fig. 1 is a vertical cross-sectional view of a basic embodiment of the preserving material according to the present invention;

Figs. 2 (A) and (B) are vertical cross-sectional views of other embodiments having small openings in a covering barrier sheet;

Figs. 3 (A) and (B) are partially cross-sectional perspective views of other embodiments in which end portions of the barrier sheets are bonded together;

Fig. 4 (A) is a perspective view of another embodiment and Fig. 4 (B) is a cross-sectional view of the same embodiment taken on the line B-B of Fig. 4 (A); and

Figs. 5 (A) and 5 (B) are vertical cross-sectional views of further modified embodiments of the preserving materials according to the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The preserving material and the method for producing the same will be described in more detail.

The adsorbent sheet used in the present invention is one member selected from the group con-

sisting of papers such as thick paper board, woven or nonwoven fabrics made of natural pulp or polyolefin threads, foamed plastics sheets, cotton wool and plastics sheets which are compatible with the preserving liquid.

The above plastics sheet which is compatible with the preserving liquid is exemplified by the copolymers of ethylene and a monomer containing a polar group such as ethylene-vinyl acetate copolymer, ethylene-ethyl acrylate copolymer and ethylene-ethyl methacrylate copolymer.

The barrier films are at least one member selected from the group consisting of thermoplastic resin films such as those made of polyolefin, polystyrene, polyamide, polyester, polyvinyl chloride, polyvinylidene chloride, saponified product of ethylene-vinyl acetate copolymer and vinyl alcohol; the thermoplastic resin films applied with metallic vacuum evaporation coating; metal foils such as aluminum foil and nickel foil; and regenerated cellulose film. As the barrier film, transparent films are preferable. When a film is printed, reverse printing is more preferable in view of food sanitation.

As the preserving liquid used in the present invention, it is possible to use lower alcohols such as methyl alcohol, ethyl alcohol and isopropyl alcohol or a mixture of these alcohols with edible organic acids, fatty acids or their esters, or polyhydric alcohols. Especially, because the preserving material is used for foodstuffs, ethyl alcohol is most preferable. When ethyl alcohol is used together with at least another kind of the above compounds such as an edible organic acid, it is possible to avoid the irritating smell and the oozing out of flavor or dyestuff caused by the use of ethyl alcohol. In addition, the effect of preservation can be much improved.

The foregoing edible organic acids are exemplified by lactic acid, malic acid, fumaric acid, citric acid, acetic acid, succinic acid, tartaric acid, gluconic acid, adipic acid, ascorbic acid and phytic acid.

The fatty acids or their esters are exemplified by formic acid, propionic acid, butyric acid, caproic acid, enanthic acid, capric acid, caprylic acid, or their esters. The polyhydric alcohols are exemplified by ethylene glycol, propylene glycol, glycerol, sorbitol, xylitol and mannitol.

The preserving material of the present invention will be described with reference to several examples shown in the attached drawings.

Fig. 1 is a vertical cross-sectional view of a basic embodiment 1 of the preserving material according to the present invention. A preserving material 1 has a layered structure which is composed of an adsorbent sheet 2 and barrier films 3 which are applied to both surfaces of the adsorbent sheet 2. The preserving liquid impregnated to the

adsorbent sheet 2 is released little by little from the peripheral edges of the layered structure.

In Figs. 2 (A) and 2 (B) are vertical cross-sectional views of modified embodiments of the preserving materials 1a of the invention. The preserving material 1a in Fig. 2 (A) is composed of an adsorbent sheet 2, a barrier film 3a on one side of the adsorbent sheet 2 and a barrier film 3b on the other side of the sheet 2. The latter barrier film 3b is provided with a plurality of small openings. In this embodiment, the preserving liquid is evaporated and released from the many small openings of the barrier film 3b as well as from the peripheral edges of the layered structure.

The preserving material 1b shown in Fig. 2 (B) is composed of an adsorbent sheet 2, and barrier films 3b and 3c on both side surfaces of the adsorbent sheet 2. Both the barrier films 3b and 3c have a plurality of small openings. In this embodiment, the preserving liquid is evaporated and released from the many small openings of the barrier films 3b and 3c as well as from the peripheral edges of the layered structure. As compared with the embodiment shown in Fig. 1, the preserving materials 1a and 1b of these embodiments are suitable for use in the case that a large rate of releasing of preserving liquid or rapid effect is required, though these depend upon the used material of the adsorbent sheet 2 and preserving liquid and upon the purposes and uses.

In the preserving material 1c shown in Fig. 3 (A), the adsorbent sheet 2 is interposed between a pair of barrier films 3 which are larger than the adsorbent sheet 2. The peripheral edges 4 of these barrier films 3 outside the adsorbent sheet 2 are thermally bonded together.

In the preserving material 1d shown in Fig. 3 (B), the adsorbent sheet 2 is covered by a sheet of barrier film 3 which is more than twice larger than the adsorbent sheet 2. The side edges 4 of the barrier film 3 are put together by thermal adhesion.

In the preserving materials 1, 1a and 1b shown in Figs. 1, 2 (A) and 2 (B), the delamination is sometimes caused to occur between the adsorbent sheet 2 and barrier films 3, 3a, 3b and 3c, which causes undesirably rapid releasing of preserving agent. However, in the embodiments 1c and 1d shown in Figs. 3 (A) and 3 (B), such delamination can be avoided because the peripheral edges of the preserving material are tightly bonded together. The delamination of this kind is liable to occur in the case that a preserving liquid contains solvents such as toluene and xylene and an adhesive agent which is soluble to such solvents is used.

Fig. 4 (A) is a perspective view of another embodiment and Fig. 4 (B) is a cross-sectional view of the same embodiment taken on the line B-B of Fig. 4 (A). The preserving material 1e is

composed of an adsorbent sheet 2, a barrier film 3a having no small opening and another barrier film 3b having a plurality of small openings 5. In addition, the peripheral edges 4 of the barrier films 3a and 3b are thermally bonded together. Also in the embodiment 1e of Figs. 4 (A) and 4 (B), it is possible to replace the barrier film 3a with a barrier film 3c as shown in Fig. 2 (B) having plurality of small openings.

Figs. 5 (A) and 5 (B) are vertical cross-sectional views of further modified embodiments of the preserving materials according to the present invention.

The layered structure of the preserving material of the embodiment 1f in Fig. 5 (A) is composed of an adsorbent sheet 2 having a plurality of small openings 5, a barrier film 3a having no small opening and another barrier film 3b having a plurality of small openings 5.

The embodiment 1g shown in Fig. 5 (B) is composed of an adsorbent sheet 2 having a plurality of small openings 5, a barrier film 3a having no small opening, another barrier film 3b having a plurality of small openings 5 and a diffusion layer 6 which is put in the space between the adsorbent sheet 2 and the barrier film 3a. The diffusion layer 6 can facilitate the evaporation of the preserving liquid. The diffusion layer 6 is generally made of paper, woven or nonwoven fabric or open cell foamed plastics. The preserving liquid in the adsorbent sheet 2 permeate into the diffusion layer 6. Thus, the preserving liquid can evaporate from the bottom surfaces of the small openings 5 (the surface of diffusion layer 6) as well as from the inside wall surfaces of the small openings 5 of adsorbent sheet 2.

In the above described embodiments, the rate of evaporation of preserving liquid can be controlled widely by the size and number of small openings 5 and the kind, thickness and combination of the layered structure.

In addition, the diffusion layer 6 can not only accelerate the evaporation of preserving liquid but also make the diffusion of impregnated preserving liquid smooth.

In other words, in the preserving materials with a barrier film 3b having many small openings 5 as shown in Figs. 2 (A), 2 (B), 4 (A) and 4 (B), the contained preserving liquid just below the openings 5 is evaporated through the small openings 5 with the passage of time. However, the preserving liquid contained in the portions far from the small openings cannot be evaporated easily and it is liable to remain in the adsorbent sheet 2. This fact is considered to be due to the large difference between the rate of diffusion of the preserving liquid in the adsorbent sheet and the rate of evaporation of preserving liquid just below the small openings.

Accordingly, in these sheets, the effect of preservation is lost before all the preserving liquid is evaporated, which reduces the life of the preserving material.

However, when the adsorbent sheet 2 is also provided with a plurality of small openings 5 and it is used in combination with the diffusion layer 6, such the disadvantage can be much improved and the wide range controlling of the rate of evaporation can be made possible.

The method for producing the preserving material of the present invention is as follows.

Barrier films are applied to both surfaces of the adsorbent sheet by means of an adhesive agent, thermal fusion or extrusion lamination to obtain a layered structure. The layered structure is preferably cut into several centimeter square pieces and they are soaked in a preserving liquid. Thus, pieces of the adsorbent sheet are impregnated with the preserving liquid from the peripheral edges of the adsorbent sheet.

Accordingly, the evaporation of the preserving liquid is caused to occur in the peripheral portions of the adsorbent sheet. The evaporation of alcohol having a relatively high evaporation rate can be thus controlled appropriately.

In the preparation of the preservation materials of other embodiments as shown in Figs. 2 (A) to 5 (B), the layered structure is made in the like manner as the above by using an adsorbent sheet having many small openings and/or barrier films having many small openings. In the cases of preserving materials 1c, 1d and 1e in Figs. 3 (A), 3 (B), 4 (A) and 4 (B), the adhesion between the respective layers is not always necessary because their peripheral edges are bonded together. The obtained layered structure is then impregnated with a preserving liquid, which preserving liquid comes into the adsorbent sheet through both the peripheral edges of the layered structure and the small openings.

The preserving material according to the present invention can be produced by a continuous process. That is, a layered structure is continuously prepared by using multi-layer free blown film technique or multi-layer casting film technique. When the obtained layered structure is free blown films, the peripheral edges of them are torn off. When the obtained layered structure is a cast film sheet, the edges are trimmed. Then these are passed through a preserving liquid vessel for a predetermined retention time and then wound up to be stored.

It is possible to control the rate of evaporation of the preserving liquid by the combined use of organic acids with alcohol and the provision of small openings in the films. The shape of preserving material can also be determined arbitrary in view of uses and type of packages, for example,

square, rectangle, triangle, circle and so forth.

In one example of use, the preserving material is made in the form of chips and they are sealed in a package together with a foodstuff, thereby filling the inside of the package with the vapor of preserving liquid.

More particularly, the preserving material of the present invention is used for preserving foodstuffs such as fresh vegetables such as tomato, cucumber, lettuce and cabbage, mushrooms, fruits such as apple, banana, strawberry, peach and pineapple, bread, cakes, meat products such as ham and sausage, marine products, noodles, and flowers such as rose, chrysanthemum and tulip.

Furthermore, oxygen absorbing agent, carbon monoxide generating agent, deodorants such as activated carbon, adsorbents such as silicon dioxide, talc, kaolin, starch can be used together within the scope of the present invention. These materials can be used, for example, putting them into the space between the adsorbent sheet and a barrier film.

In addition, aromatic substances (natural and synthetic perfumes, spices, flowers and green leaves) can also be used together. As described above, the preserving material of the present invention is characterized in that it can be produced without difficulty, the soaking in a preserving liquid is easily done in a short time, the packing together with foodstuffs is also easy, and the taste and quality are not deteriorated because both surfaces of adsorbent sheet are covered by barrier films and the preserving liquid is not brought into direct contact with foodstuffs.

Especially in the use of alcohol which evaporates rapidly, the rate of evaporation of the preserving liquid can be easily controlled because the preserving liquid is evaporated and released from only the peripheral edges and, in some embodiments, from the small openings of barrier films.

The present invention will be described in more detail with reference to examples.

#### Example 1

Nonwoven fabric made of natural pulp of 2 mm in thickness and 500 g/m<sup>2</sup> in basis weight was cut into adsorbent sheets of 4 x 5 cm. Polyethylene films of 50 micron in thickness were thermally bonded to both surfaces of the adsorbent sheet to prepare an adsorbent material of the present invention.

This chip was soaked in ethyl alcohol, wherein the chip was saturated with ethyl alcohol within 5 seconds. The quantity of adsorbed ethanol was 2 g (1 g of adsorbent sheet adsorbed 2 times by

weight of alcohol).

This preserving material was sealed in a package together with 600 g of bread. The rate of evaporation of ethanol was 50% per 24 hours.

This package was left as it stands for 1 month but the bread did not gather mold.

#### Comparative Example 1

Ethanol was adsorbed by 4 g of silicon dioxide, which was saturated with 2 g of ethanol (a half by weight of the silicon dioxide).

This was put into a small paper bag and sealed in a container together with 600 g of bread. Whole the ethanol was evaporated within 8 hours.

There occurred nothing after 2 weeks, however, the bread gathered mold after 1 month.

#### Comparative Example 2

Only the adsorbent sheet used in Example 1 was soaked in ethyl alcohol. 2 g of alcohol was adsorbed within 2 seconds.

This was sealed in a package together with 600 g of bread. The rate of evaporation of ethanol was 100% after 1 hour.

The bread did not gathered mold after 1 month but it gathered mold after 2 months.

#### Example 2

The adsorbent material in Example 1 was used to adsorb 2 g of preserving liquid consisting of 95% of ethanol and 5% of acetic acid to prepare a preserving material. This was sealed in a package together with 600 g of bread.

The rate of evaporation was 50% after 24 hours. After 2 months' storage, the bread gathered no mold.

#### Claims

1. A preserving material having a multilayer structure comprising an impregnated adsorbent sheet which contains a preserving liquid and barrier films impermeable to said preserving liquid and which are applied to both surfaces of said impregnated adsorbent sheet, wherein the components of said preserving liquid can evaporate little by little at least from the peripheral edges of the preserving material.

2. The preserving material of Claim 1, wherein at least one of said barrier films is provided with a plurality of small openings.

3. The preserving material of Claim 1 or 2, wherein the peripheral edges of said barrier films are bonded together.

4. The preserving material of any of the Claims 1 to 3, wherein at least one of said barrier films has a plurality of small openings and the peripheral edges of both of the barrier films prolonged outside the impregnated adsorbent sheet are thermally bonded together.

5. The preserving material of any of the Claims 1 to 4, wherein said impregnated adsorbent sheet has a plurality of small openings and at least one of said barrier films also has a plurality of small openings.

6. The preserving material of any of the Claims 1 to 5, wherein the adsorbent sheet of said impregnated adsorbent sheet is made of a material selected from the group consisting of paper, non-woven fabric, cotton wool, foamed plastics or plastic sheet which is compatible with said preserving liquid.

7. The preserving material of any of the Claims 1 to 6, wherein said barrier film is made of a material selected from the group consisting of polyolefin, polystyrene, polyamide, polyester, polyvinyl chloride, polyvinylidene chloride, saponified product of ethylene-vinyl acetate copolymer, polyvinyl alcohol, and aluminum foil.

8. The preserving material of any of the Claims 1 to 7, wherein said preserving liquid contains at least a lower alcohol.

9. The preserving material of Claim 8, wherein said preserving liquid is a mixture of ethanol and a fatty acid or its ester.

10. A method for producing a preserving material according to Claim 1 which consists of the steps of :

previously applying barrier films to both surfaces of an adsorbent sheet; and

soaking the obtained layered material in a preserving liquid, thereby impregnating the adsorbent sheet with the preserving liquid from peripheral edge portions of the layered material.

11. The method of Claim 10, wherein a preserving material having the characteristics according to any of the Claims 2 to 9 is produced.

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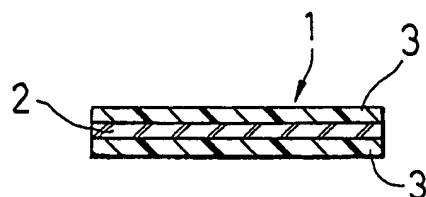
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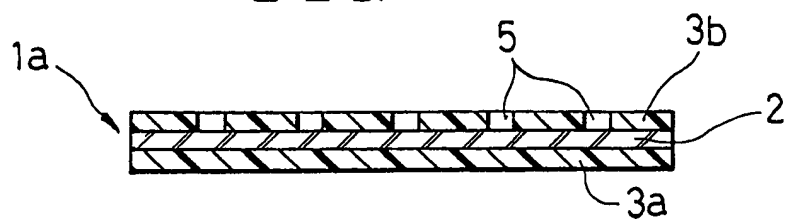
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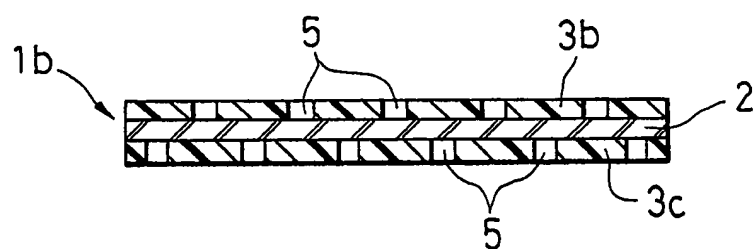
**FIG. 1**



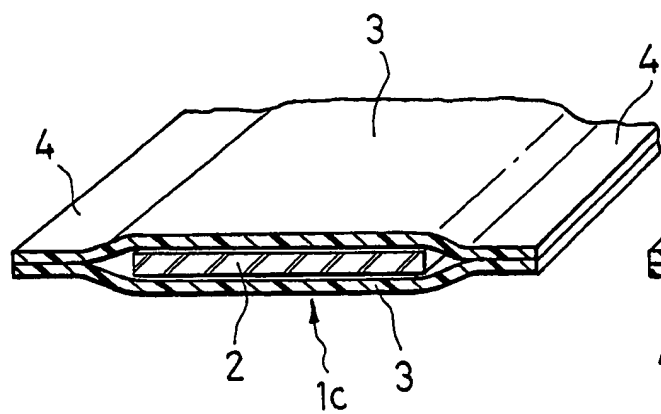
**FIG. 2(A)**



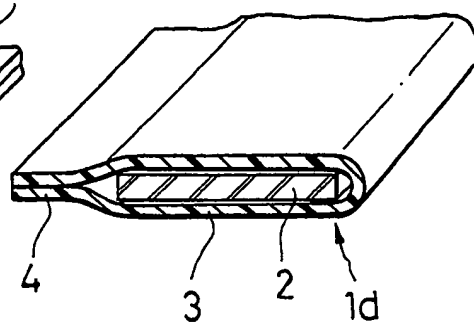
**FIG. 2(B)**



**FIG. 3(A)**

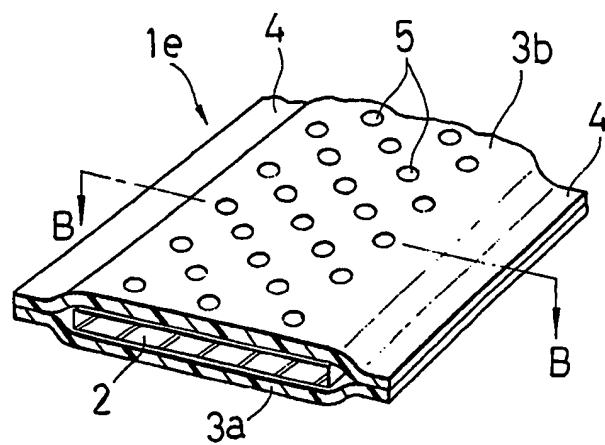


**FIG. 3(B)**

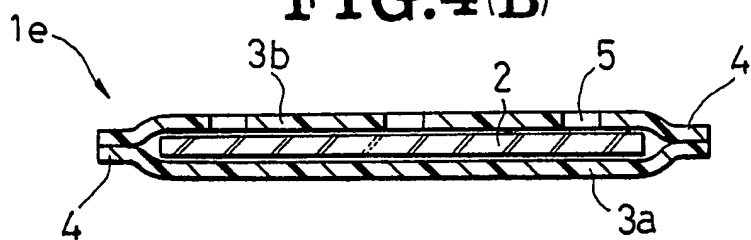




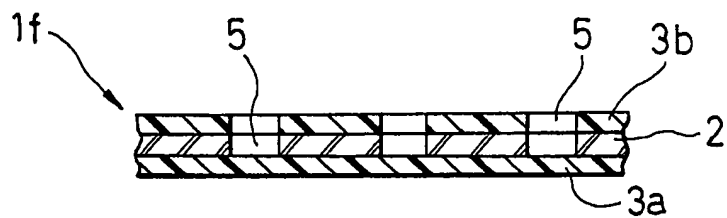
**FIG.4(A)**



**FIG.4(B)**



**FIG.5(A)**



**FIG.5(B)**

